

FIG. 1. Plot of surface-potential configuration on the right and observed ion energy distribution on the left for H_2 molecules with an applied field of approximately 2.5 V/\AA . The ion distribution is shifted from ΔE (the energy deficit from surface potential) by I , the ionization potential, so that the features are aligned with the pertinent level. The potential distribution with an atom (of $I = 15.6 \text{ eV}$) present is drawn in dashed lines. Extrapolation of the potential energy (not including the atomic field) to the surface defines E_0 . Locations of the first five stationary states of the infinite triangular well are also shown. The scale in the center is in electron volts and applies to both sides.

the surface states depend on the field rather than the crystal lattice.

The conventional model of a surface, with an atom near that surface, in an electric field is shown in Fig. 1. Low-energy electrons tunneling into the roughly triangular well outlined in the figure have a certain probability of being reflected by the metal surface.² That such reflectivity exists can be empirically demonstrated by the familiar difficulty of collecting low-energy electrons; special means such as a Faraday cage must be used for quantitative collection. If the reflectivity is unity and tunneling back to the atom is unlikely, well-defined energy levels will exist within the well. Lower reflectivities will result in short-lived states and consequent level broadening.

Alternately, the problem may be described in terms of the matching of wavefunctions at the boundaries of the three regions of interest: the atom, the triangular well, and the surface. The probability amplitudes in the region of linearly increasing potential are given in terms of Airy functions³ and are initially unspecified in amplitude and phase. These two parameters are fixed by equating logarithmic derivatives at the boundaries and result in small amplitudes in the well except at energies near the eigenvalues of the simple infinitely high triangular well. Consequently, low tunneling rates are expected for atomic levels not aligned with the well levels. The presence of the atomic potential and associated image force acts as a small perturbation on the well levels. A calculation using square potentials verifies this picture; a square well open on one side to a higher-energy continuum demonstrates resonances at energies very near to the closed-well eigenvalues.

Eigenvalues E_n of the infinite triangular well are given by the relation

$$-(2m/\hbar^2 e^2 F^2)^{1/3} E_n = a_n,$$

where m is the electronic mass, e the electronic charge, F the field, and a_n the n th root of the particular Airy function which is finite for all real values of its argument. To complete a rough correspondence with our picture, we must add to E_n a quantity E_0 given by the difference between the Fermi energy and the energy at which the extrapolated field curve intersects the surface. Results of this calculation and an observed distribution are compared in Fig. 1. Good agreement is not expected for the first level because of the influence of the image potential which is not included in the above calculation and because of the sensitivity of this level to the assumed surface configuration. The calculated variation of peak spacings with electric field agrees closely with experimental values and, over the energy range observable, is very nearly indistinguishable from a first-power field dependence.

In addition to the main structure explained above, the experiments show further detail in peak structures indicative of the nature of the surface and surface reactions. It is expected that this type of analysis will be useful in surface studies. For example, it is to be noted that a pure surface reaction such as H_3^+ formation exhibits no secondary structure.¹

The model described here is simplified and lacking in detail but is believed to be essentially correct. A more thorough analysis and presentation of data will be submitted at a later date.

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¹ A. J. Jason, R. P. Burns, and M. G. Inghram, *J. Chem. Phys.* **43**, 3762 (1965).

² For example, I. Gimpel and O. Richardson, *Proc. Roy. Soc. (London)* **A182**, 17 (1943).

³ L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 70.

Energy Threshold for $D + H_2 \rightarrow DH + H$ Reaction*

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WE have been able to measure the threshold energy E_0 for the reaction $D + H_2 \rightarrow DH + H$. The value obtained was $(0.33 \pm 0.02) \text{ eV}$. Apparently, this is the first direct determination of a threshold energy for a reaction involving the formation and breaking of covalent bonds.

The method used consists of photolyzing a mixture of DI or DBr plus H_2 with monochromatic light and determining the wavelength dependence of the resulting

$[\text{DH}]/[\text{D}_2]$ concentration ratio. The photodissociation of DI produces translationally hot D atoms¹⁻⁴ capable of reacting with H_2 at room temperature. Light in the wavelength interval 3660 to 3030 Å excites DI from its ground electronic state $^1\Sigma^+$ to the repulsive state $^3\Pi_1$ from which it dissociates into ground state $^2P_{3/2}^0$ iodine and $^2S_{1/2}$ deuterium atoms.⁵ The minimum energy needed to product excited $^2P_{3/2}^0$ iodine atoms⁶ corresponds to a wavelength of 3130 Å. However, even at 3030 Å, the contribution of this state is probably unimportant. Therefore, in the wavelength region mentioned, the photon energy in excess of the DI bond dissociation energy ($D_0^0 = 3.098$ eV) appears as translational energy of the fragments, most of it (98.5%) in the D atoms. It is thus possible to produce essentially monoenergetic D atoms with translational energies relative to the H_2 in the range of 0.14 to 0.48 eV. Photolyzing DBr at 2537 Å extends this range to 0.53 eV since the dipole strength for transitions from ground-state DBr to excited states which dissociate into excited $^2P_{3/2}^0$ bromine atoms is quite low.⁵ The hot D atoms produced can, if sufficiently energetic, react with H_2 to form DH and H. The D atoms that escape this reaction react with DI to form D_2 .

The experimental equipment consisted of a mercury lamp, a monochromator, a Teflon-lined photolysis vessel, and a thermopile. Mixtures of DI or DBr and H_2 of different concentration ratios were photolyzed at room temperature or at 196°K. The $[\text{D}_2]/[\text{DH}]$ ratio was then determined with a special double-collector hydrogen isotope-ratio mass spectrometer.⁷ Plots of $[\text{D}_2]/[\text{DH}]$ versus $[\text{DI}]/[\text{H}_2]$ were linear, and the nonvanishing nature of their intercepts was attributed^{3,4} to the hot D-atom reaction with H_2 . Similar experiments with DI or DBr and He mixtures also furnished straight lines of $[\text{D}_2]/[\text{DH}]$ versus $[\text{DI}]/[\text{He}]$ due to the presence of a small amount (2% to 4%) of HI or HBr impurity.

In Fig. 1 we have plotted, as a function of the average initial energy E_i of the D atoms relative to the H_2 molecules, the difference $\Delta = ([\text{DH}]/[\text{D}_2])_{\text{H}_2} - ([\text{DH}]/[\text{D}_2])_{\text{He}}$, where the $([\text{DH}]/[\text{D}_2])_{\text{He}}$ refer to the reciprocals of the linear intercepts mentioned above. The values of E_i include small thermal contributions (of about 0.03 eV). Consideration of thermal rate constants shows unequivocally that the D atoms that escape the hot reaction with H_2 and become thermalized do not form DH since they react exclusively with DI to form D_2 even at the lowest $[\text{DI}]/[\text{H}_2]$ ratios used in our experiments. This conclusion is confirmed by the equality of the results at 196°K and room temperature. Therefore, Δ is a measure of the DH formed by this hot reaction plus that formed by reaction of the resultant H atoms with DI.⁸ Consequently, when E_i equals the threshold energy, Δ vanishes. From Fig. 1 we thus obtain $E_0 = (0.33 \pm 0.02)$ eV.⁹ The error is a rough estimate based on the bandpass of the monochromator and the accuracy of the analyses.

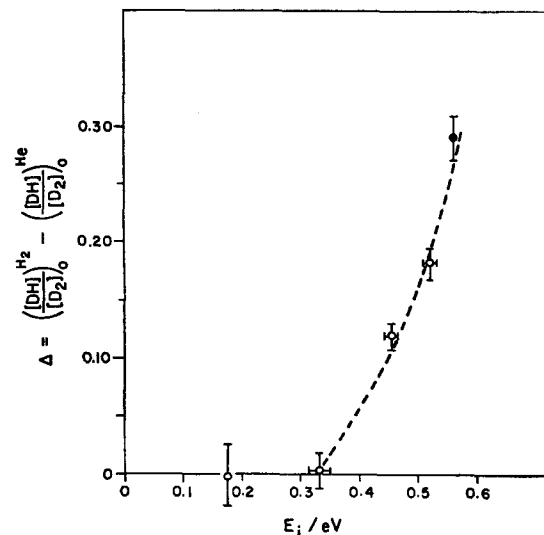


FIG. 1. Effect of average relative initial kinetic energy of reactants of $\text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H}$ reaction. Open circles: photolysis of DI mixtures at 3660, 3340, 3130 and 3030 Å, in order of increasing energies. Full circle: photolysis of DBr at 2537 Å.⁸

Using the method of classical trajectory calculations,¹⁰ and a semiempirical potential-energy surface,¹¹ Karplus *et al.*¹² recently obtained a value of 0.26 eV for the rotationally averaged E_0 .⁹ Micha,¹³ using an approximate quantum-mechanical method and a different potential-energy surface, obtained a value of $E_0 = 0.23$ eV for the $J=0$ to $J'=0$ reaction.

We are presently performing additional experiments of higher accuracy. We are also attempting to extract the energy dependence of the rotationally averaged⁹ reaction cross section from the data. Using assumed but reasonable elastic and reactive cross sections, we have obtained preliminary numerical solutions of a Boltzmann equation pertinent to our experimental conditions. They furnished theoretical $[\text{DH}]/[\text{D}_2]$ ratios which are of the right order of magnitude and sensitive to the assumed cross sections.

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‡ Contribution No. 3035.

¹ R. A. Ogg, Jr., and R. R. Williams, Jr., *J. Chem. Phys.* **13**, 586 (1945).

² H. H. Schwarz, W. H. Hamill, and R. R. Williams, Jr., *J. Am. Chem. Soc.* **74**, 6007 (1952).

³ R. J. Carter, W. H. Hamill, and R. R. Williams, Jr., *J. Am. Chem. Soc.* **77**, 6457 (1955).

⁴ (a) R. M. Martin and J. E. Willard, *J. Chem. Phys.* **40**, 2999 (1964); (b) p. 3007.

⁵ (a) R. S. Mulliken, *Phys. Rev.* **51**, 310 (1937); (b) *J. Chem. Phys.* **8**, 382 (1940).

⁶ C. E. Moore, *Atomic Energy Levels* (U.S. Department of Commerce, National Bureau of Standards, Washington, D.C., 1958), Vol. 3, p. 106.

⁷ C. R. McKinney, J. M. McRea, S. Epstein, H. A. Allen, and H. C. Urey, *Rev. Sci. Instr.* **21**, 724 (1950). We are extremely grateful to Professor Samuel Epstein for permitting us to use his instrument at the California Institute of Technology.

⁸ The point obtained using DBr and 2537-Å light should not be included in Fig. 1 without a correction which takes into account the presently unknown differences in the thermal rate constant ratio of the reactions $H+DX \rightarrow HD+X$ and $H+DX \rightarrow HX+D$ for $X=I$ and $X=Br$. This correction would slightly lower or raise the curve of Fig. 1 around $E_0=0.55$ eV, but would not affect E_0 .

⁹ At room temperature practically only the ground vibrational state of H_2 is populated, but several of its rotational states contribute to the reaction. Therefore, the reaction cross section and threshold energy corresponding to these experiments refer to a rotational average at this temperature.

¹⁰ M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* **42**, 1105 (1965) and references therein.

¹¹ M. Karplus and R. N. Porter, *J. Chem. Phys.* **40**, 1105 (1964).

¹² M. Karplus, R. N. Porter, and R. D. Sharma (private communication).

¹³ (a) D. A. Micha, *Arkiv Fysik* **20**, 411 (1965); (b) p. 425; (c) p. 437.

Phosphorescence of $K_3Co(CN)_6$

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THE complex ions of only a few of the transition metals have been found to luminesce,¹ with most of the data referring to the phosphorescence of d^3 ions, particularly of chromium(III).^{2,3} We report here our observation of the emission spectrum of potassium hexacyanocobaltate(III).

One other example of luminescence of d^6 complexes, the tris(dipyridyl) and tris(phenanthroline) ruthenium(II) salts, is known,⁴ and has been characterized as fluorescence.⁵ On the basis of the lifetime of the emission, ~ 10 μ sec, and of the position of the emission bands, Crosby *et al.* make the assignment of this transition to ${}^1T_1 \rightarrow {}^1A_1$.

The emission spectrum of crystalline $K_3Co(CN)_6$ was measured with a Jarrell-Ash 0.5-m $f/6.3$ grating spectrograph (20 Å/mm in first order) on Kodak 1N plates. Excitation was front surface with ultraviolet radiation from a mercury arc. A broad band with a maximum at 14 400 cm^{-1} and a half-width of about 2000 cm^{-1} was observed with the crystal at 4.2° and at 77°K. The luminescence is distinctly visible as a red glow; in fact, it can be seen even with the crystal at room temperature, although it is then quite weak. This band seems to be devoid of structure; however, because of the uneven spectral sensitivity of 1N plates in the red, this point is uncertain. Qualitative observations of the lifetime by the phosphoroscope technique indicate a value of about 10^{-8} sec.

In solution, there are three principal bands found in the absorption spectrum.⁶ At 50 000 cm^{-1} , there is a very intense band, with $\epsilon_{max}=1.6 \times 10^4$. Two weaker bands appear at 32 100 cm^{-1} ($\epsilon_{max}=180$) and at 38 600 cm^{-1} ($\epsilon_{max}=160$). We have found, in addition, a weak band centered at about 18 500 cm^{-1} , which could be seen only with a crystal, because it is masked by the tail of the more intense ultraviolet band in solu-

tion. The extinction coefficient at the band maximum is approximately 0.01.

According to the calculations of Tanabe and Sugano,⁷ the low-lying electronic states in a d^6 , low-spin octahedral complex are, in order of increasing energy: ${}^1A_{1g}(t_{2g}^6)$, the ground state, ${}^3T_{1g}(t_{2g}^5e_g^1)$, ${}^3T_{2g}(t_{2g}^5e_g^1)$, ${}^1T_{1g}(t_{2g}^5e_g^1)$, and ${}^1T_{2g}(t_{2g}^5e_g^1)$. The two bands of the absorption spectrum which lie in the near ultraviolet can reasonably be assigned to the transitions ${}^1T_{2g} \leftarrow {}^1A_{1g}$ (38 600 cm^{-1}) and ${}^1T_{1g} \leftarrow {}^1A_{1g}$ (32 100 cm^{-1}). They have about the expected extinction coefficients and the correct relative energies for this assignment.

The weak absorption band probably represents the lowest energy transition: ${}^3T_{1g} \leftarrow {}^1A_{1g}$ (18 500 cm^{-1}), although its intensity is somewhat low. From the bandwidth and extinction coefficient, the natural lifetime of the ${}^3T_{1g}$ state should be of the order of 0.1 sec. The mirror-image relationship of the observed emission band together with the long lifetime of the luminescence makes this assignment reasonable. Hence, the emission arises from the same transition, ${}^3T_{1g} \rightarrow {}^1A_{1g}$, and, since it is spin forbidden, is phosphorescence.

A more detailed analysis of these band systems will be published in the near future.

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¹ See G. B. Porter and H. L. Schläfer, *Z. Elektrochem.* **68**, 316 (1964), for references.

² G. B. Porter and H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)* **40**, 280 (1964).

³ L. E. Forster and K. DeArmond, *Spectrochim. Acta* **19**, 1403, 1687 (1963).

⁴ J. P. Paris and W. W. Brandt, *J. Am. Chem. Soc.* **81**, 5001 (1959).

⁵ G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.* **43**, 1498 (1965).

⁶ A. Kiss and M. Czegléd, *Z. Anorg. Chem.* **235**, 407 (1938).

⁷ Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954).

Muonium Chemistry*

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MUONIUM (M) is the atom consisting of a positive muon and an electron, and it will behave as a light isotope of hydrogen with regard to its atomic interactions and chemical reactions since the muon mass is 207 times the electron mass and since the muon mean lifetime of 2.2 μ sec is long compared to electron atomic orbital times. The present Letter reports on two methods for studying muonium chemistry and on initial results for the interactions of muonium with a number of molecules.¹

The methods utilize the powerful techniques of elementary particle physics and rely upon parity non-conservation in the weak interactions responsible for the production and decay of the muon. From the decay of positive pions, polarized positive muons are produced, and in the decay of positive muons into positrons